atoms of the coordinated allyl group of the other ring. Electrophilic attack of the latter on the former then generates bond C(4)–C(1′), leaving a residual positive charge on C(5). A second electrophilic attack then occurs, of C(5) on C(5′), one of the coordinated alkenes of the second ring. Once bond C(5)–C(6′) is formed, Rh′ is σ-bonded to C(7′) and η^4-bonded to the butadiene fragment C(2′)–C(5′).

As noted above, this reaction sequence can only occur with diastereoisomer **2b-A**. In this case, the formation of the two C–C bonds, C(4)–C(1′) and C(5)–C(6′), results in two new seven-membered rings, C(1)C(2)C(3)C(4)C(1′)C(8′)C(8) and C(5)C(6)C(7)C(8)C(8′)C(7′)C(6′). A similar sequence beginning with **2b-B** would generate new six- and eight-membered rings in a more strained polycyclic structure. We conclude, therefore, that diastereoisomer **2b-B** (the minor component, shown by ^{1}H NMR spectroscopy) is slowly converted to **2a-A** and then to **5**.

Acknowledgment. We thank the SERC for research studentships to L.B. and J.B.S., the National Science Foundation (CHE 83-08974 and CHE 86-03728) and N. A.T.O. for financial support, and Johnson Matthey for a generous loan of rhodium trichloride. We also thank Dr. R. J. Goodfellow for valuable help with the assignment of the ^{1}H NMR spectrum of complex **5**.

Registry No. **2b**, 113706-13-1; **3**, 55480-71-2; **4**, 113706-11-9; **5**, 113725-95-4; **6**, 55480-76-7; **8**, 89958-69-0; $[Rh(\mu\text{-}Cl)(\eta^4\text{-}Cot)]_2$, 12308-49-5; TlCp, 34822-90-7; $[\#\text{-}Bu_4N][BPh_4]$, 15522-59-5; $[n\text{-}Bu_4N]Br$, 1643-19-2; $Na[BPh_4]$, 143-66-8; $[FeCp_2][PF_6]$, 11077-24-0; $[(\eta^2,\eta^3{:}\sigma',\eta^4\text{–}C_{16}H_{16})Rh_2Cp_2][BPh_4]_2$, 113747-48-1.

Supplementary Material Available: Full tables of bond lengths and angles (Table II), atomic coordinates (Table IV), and atomic displacement parameters for compound 5 (9 pages); a listing of structure factors for compound 5 (31 pages). Ordering information is given on any current masthead page.

Cycloaddition Reactions of Tetrafluorodisilacyclobutene with Conjugated Dienes Mediated by Metal Carbonyls. 4. Stereoselective 1,4-Addition and Conformations of 1,4-Disilacycloocta-2,6-dienes

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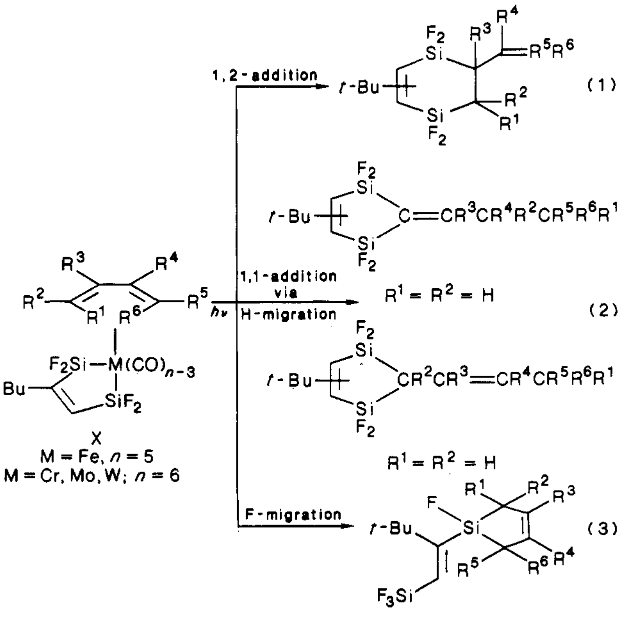
Received October 23, 1987

Cycloaddition reactions between 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) and various conjugated dienes mediated by $Ni(CO)_4$ have been studied. The reactions proceed via a (η^4-diene)disilametallacycle intermediate that decomposes to result in the stereoselective 1,4-addition products, 1,4-disilacycloocta-2,6-dienes. Variable-temperature ^{19}F NMR study of one derivative of the 1,4-disilacycloocta-2,6-dienes (**2i**) shows that it exists in a chair form in solution. Compound **2i** undergoes chair to chair interconversion, with free energy of activation, $\Delta G^\ddagger = 10.5 \pm 0.1$ kcal/mol.

We recently reported in a series of papers the transition-metal carbonyl mediated cycloaddition reactions between disilacyclobutenes and conjugated dienes, carried out under photochemical conditions.[1-5] With use of different metal carbonyls (M = Fe, Cr, Mo, W) and substituted dienes, the reaction intermediate X was shown to proceed via different reaction pathways, eq 1–3.

Since the reaction pathways can be controlled by the geometry of X,[1] the electronic properties of the central metal,[3] and the steric effects of the substituents,[2] a model of "fine-tuning" can be demonstrated. For example, in the reaction of cyclohexadiene, the geometry of the intermediate $F_2\overline{Si(t\text{-}Bu)C{=}CHSiF_2M}(\eta^4\text{-}C_6H_8)(CO)_{n-3}$ allows both SiF_2 groups to make the initial attack in the case of M = Fe but allows only one SiF_2 group to make the initial attack in the case of M = W.[1] Also, under the same reaction conditions, F-migration is the preferred reaction pathway when hard metals are used (i.e., M = Cr), whereas



H-migration goes with softer metals such as W and Fe.[1,3]

Interestingly, the most commonly observed reaction pathway, namely, 1,4-addition to the conjugated dienes was not observed in these reactions. The Pd- and Pt-mediated cycloaddition reactions between disilabutenes and conju-

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(1) Lin, C. H.; Lee, C. Y.; Liu, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 1323.

(2) Part 1: Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics* **1987**, *6*, 1861.

(3) Part 2: Lee, C. Y.; Lin, C. H.; Liu, C. S. *Organometallics* **1987**, *6*, 1869.

(4) Part 3: Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics* **1987**, *6*, 1878.

(5) Chen, Y. C.; Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics* **1987**, *6*, 1882.

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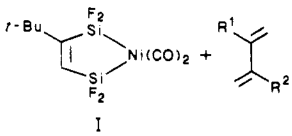
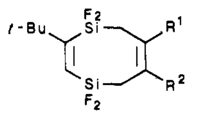
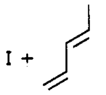
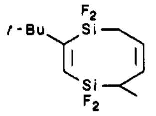
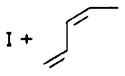
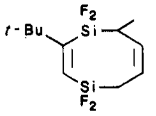
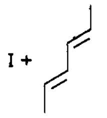
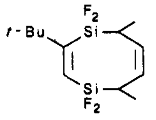
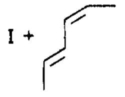
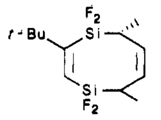
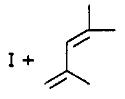
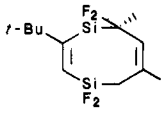
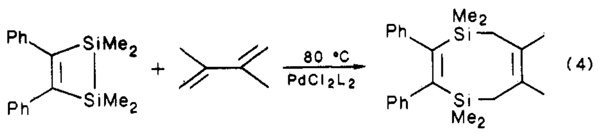
Table I. Ni-Mediated Cycloaddition Reactions between 1 and Various Conjugate Dienes

reactns	conditns	products (yield, %)
 I	−30 °C	 2a: $R^1 = R^2 = H$ (80) b: $R^1 = R^2 = CH_3$ (80) c: $R^1 = H, R^2 = CH_3$ (40) d: $R^1 = CH_3, R^2 = H$ (40)
	−30 °C	 2e (65)
	−30 °C	 2f (70)
	−30 °C	 2h (65)
	−30 °C	 2g (65)
	−30 °C	 2i (50)

gated dienes have been reported by Sakurai et al. to proceed exclusively via 1,4-additions,[6,7] for example, eq 4.



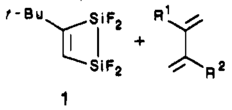
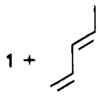
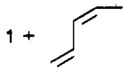
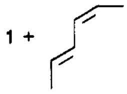
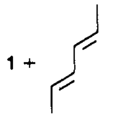
It is possible that our results reflect the crowdedness of coordination sphere of X (six-coordinate in the case of Fe and seven-coordinate in the case of Cr, Mo, and W) which hampers the second SiF$_2$ group in its attack on C$_4$ of the diene. For this reason, we chose Ni(CO)$_4$ as the mediator, which would form a less crowded four-coordinate intermediate X, for comparison. Besides, Ni is considered a softer metal than Fe. The competitive reaction pathways of direct cycloaddition vs H-migration may be studied.

This paper reports the results of the cycloaddition reactions between 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene with different 1,3-butadiene derivatives, mediated by Ni(CO)$_4$.

Results and Discussion

The experimental conditions and results of the Ni-mediated cycloaddition reactions between 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) and various conjugate dienes are summarized in Table I. These reactions can in principle be carried out either by reacting 1, Ni(CO)$_4$, and the diene together or by reacting 1 and Ni(CO)$_4$ to form the disilametallacycle I first, followed by reaction with the diene. Since the former procedure may in some cases result in considerable oligomerization of the dienes, the latter procedure was preferred.

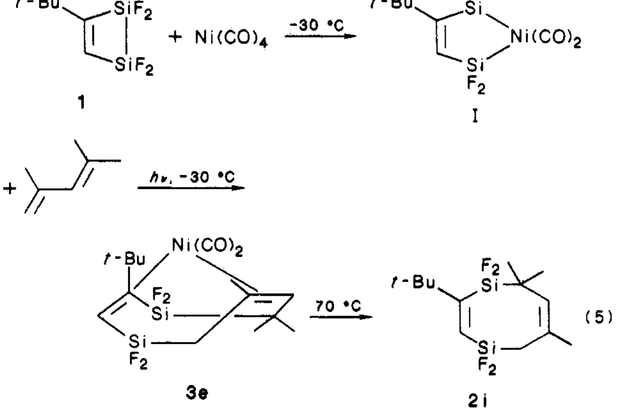
Table II. Cycloaddition Reactions between 1 and Various Conjugate Dienes without Ni Mediation

reactns	conditns	products (yield, %)
	120 °C	**2a**: $R^1 = R^2 = H$ (50) **2b**: $R^1 = R^2 = CH_3$ (40) **2c**: $R^1 = H, R^2 = CH_3$ (25) **2d**: $R^1 = CH_3, R^2 = H$ (25)
	120 °C	**2e** (15) **2f** (10)
	120 °C	**2e** (10) **2f** (15)
	120 °C	no 1,4-addition product
	120 °C	no 1,4-addition product

In general, these reactions mediated by Ni(CO)$_4$ proceed much faster than the same reactions mediated by Fe(CO)$_5$ and group 6 metal carbonyls. In most cases, the reactions went to completion instantaneously even at low temperature (−30 °C). For comparison, the thermal reactions between 1 and some of the dienes carried out without metal carbonyl mediation are listed in Table II.

These reactions, with and without metal mediation, gave primarily the products of 1,4-addition. However, it is obvious from Tables I and II that metal mediation enhances the yield and selectivity of products under much milder conditions. For example, without Ni-mediation no product of 1,4-addition was obtained in the reaction of *trans,trans*-1,3-hexadiene, whereas the Ni(CO)$_4$-mediated reaction gave a 65% yield of a stereoselective product, **2h**.

Products from 1,4-addition, designated by 2, are characterized by elemental analyses, mass spectra, and ^{1}H, ^{19}F and ^{13}C NMR spectroscopies. We chose compound 2i as an illustrative example.



Disilametallacycle I reacted with 2,4-dimethyl-1,3-pentadiene at −30 °C to give a 65% yield of (η^4-C$_{13}$H$_{22}$Si$_2$F$_4$)Ni(CO)$_2$ (**3e**), which was converted quantitatively to **2i** by heating at 70 °C.

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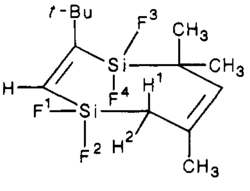
(6) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43.

(7) Sakurai, H.; Kamiyama, K.; Nakadaira, Y. *Chem. Lett.* **1975**, 887.

Compound **2i** shows satisfactory elemental analysis and mass spectrum for the formula of $C_{13}H_{22}Si_2F_4$. The ^1H NMR shows in addition to the singlet resonances at δ 1.12, 1.19, and 1.71, respectively, for the methyl protons in *t*-Bu, $-C(CH_3)_2-$, and $=CCH_3-$ groups, a doublet of doublets at δ 2.15 assigned to the methylene protons, and a resonance at δ 4.93 (s) and 6.45 (t, t) for the two olefinic protons belonging to $=CHC(CH_3)_2-$ and $=CHSiF_2-$, respectively.

The $^{13}C\{^1H\}_{BB}$ NMR spectrum of **2i** consists of six sharp lines without F coupling at δ 24.61, 26.37, 29.35, 39.66, 127.73, and 133.30 which are assigned to $-C(CH_3)_2-$, $=CCH_3-$, $-C(CH_3)_3-$, $-C(CH_3)$, $=CCH_3-$, and $=CHC(CH_3)_2-$, respectively. There are four other resonances with F coupling at δ 18.80 (t), 23.91 (t), 131.36 (t), and 168.98 (t, t) due to $-C(CH_3)_2-$, $-CH_2-$, $=CHSiF_2$, and $=C(t\text{-Bu})-$, respectively. In the $^{13}C\{^1H\}_{CW}$ spectrum, the resonances at δ 133.30 ($=CHC(CH_3)_2-$) and 131.36 ($=CHSiF_2-$) further split into doublets whereas the triplet at 18.80 (CH_2) splits into a triplet of triplets. These spectral features fit the structure of a disialcyclooctadiene perfectly.

The $^{19}F\{^1H\}$ NMR spectrum of **2i** at room temperature consists of a sharp peak at 127.43 ppm and a broadened peak at 138.12 ppm, with equal intensity. However, at -80 °C, the $^{19}F\{^1H\}$ spectrum shows two sets of AX spectrum at 126.11, 128.20 and 127.26, 144.93 ppm, respectively. An F–F homonuclear decoupling experiment confirms that these two AX spectra are caused by the geminal couplings in the two SiF_2 groups. Comparing with the nondecoupled ^{19}F NMR spectrum of **2i** taken at -80 °C, it is obvious that the resonance at 126.11 ppm involves two large F–H couplings, 18 and 9.8 Hz, respectively. The former can only be attributed to the coupling between the neighboring F^2 and H^1 which make a nearly zero dihedral angle; the latter is certainly due to the coupling with the neighboring olefin proton. This will put the SiF_2 group of 126.11 and 128.20 ppm in a position adjacent to both $=CH$ and $-CH_2-$ moieties; the structure is then **2i**. In consistence with this, the resonance of the other fluorine in this SiF_2 group, (F^1, 128.20 ppm) as well as the resonances of the other SiF_2 group (F^3, F^4, 127.26 and 144.93 ppm), all show smaller H–F couplings.



2i

A molecular model of **2i** reveals that only the chair conformation of the eight-membered ring would have the spacial arrangement of the fluorines and methylene hydrogens as required above. A boat conformation would place the two hydrogen atoms in the methylene group parallel to the two fluorine atoms in the adjacent SiF_2 group, respectively, so that each hydrogen would strongly couple with one fluorine of nearly zero dihedral angle. This analysis strongly suggests that **2i** at -80 °C exists in the chair conformation.

Comparing the $^{19}F\{^1H\}$ NMR spectra of **2i** at room temperature and -80 °C, it is obvious that **2i** undergoes dynamic structural change at a rate comparable to the NMR time scale. A variable-temperature experiment shows that the AX resonances at 126.11 and 128.20 ppm coalesce at -51.1 °C and those at 127.26 and 144.93 ppm coalesce at -21 °C.

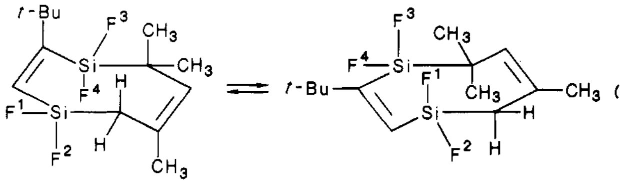
From the spectral changes at various temperatures, it can be seen that the dynamic process involved is a simple one that allows the simultaneous exchange of chemical environments of $F^1 \rightleftharpoons F^2$ and $F^3 \rightleftharpoons F^4$. This is further confirmed by estimating the free activation ΔG^*, of the dynamic process by using two coalescence temperatures mentioned above; both give $\Delta G^* = 10.5 \pm 0.1$ kcal/mol.

The same conclusion can be obtained from a detailed analysis of low-temperature-limiting ^1H NMR spectrum of **2i**. The ^1H NMR spectrum of **2i** taken at -80 °C differs from the room-temperature spectrum in two respects: (i) the singlet at δ 1.19 assigned to the two methyl groups of $-C(CH_3)_2-$ splits into two lines and (ii) the doublet of doublets at δ 2.15 assigned to the $-CH_2-$ group disappears but two complex new peaks appear at δ 2.55 and 1.75 (overlapped with the peak at δ 1.71 for $=CCH_3-$). The former appears to be a broadened triplet (18 Hz).

These observations indicate that at -80 °C, the two methyl groups in $-C(CH_3)_2-$ and the two hydrogens in $-CH_2-$ become nonequivalent, just as a puckered ring structure requires. The two singlets for $-C(CH_3)_2-$ coalesce at approximately -63 °C, and the two complex peaks coalesce at -35 °C. On the basis of the latter T_c, an free energy of activation, $\Delta G^* = 10.7$ kcal/mol, is estimated, in good agreement with the value obtained from the ^{19}F NMR spectrum (Figure 1).

At -80 °C, the broadened triplet at δ 2.55 became a broadened doublet (18 Hz) when the other broadened peak at δ 1.75 was irradiated. This strongly indicates that the broadened triplet was composed of one H–F coupling of 18 Hz and a geminal H–H coupling of approximately the same magnitude. Again, this fits the requirement of a chair form. Consequently, the peaks at δ 2.55 and 1.75 are assigned to the axial and equatorial hydrogens of the methylene group, namely, H^1 and H^2, respectively.

Because the low limiting spectrum suggests that **2i** exists in the chair conformation and because the dynamic process involves the fluxional behavior of one single species, the process is best rationalized by a chair to chair conformation interconversion (eq 6).



(6)

It is interesting to note that the dynamic behavior of cycloocta-1,5-dienes has been a complex and controversial problem.[8,9] At least three mechanisms can in principle be responsible for such processes: (i) stepwise chair to boat to chair, (ii) direct boat to boat, and (iii) direct chair to chair mechanisms. For example, the first two mechanisms have been used to interpret the dynamic NMR of dibenzocycloocta-1,5-diene.[8] The third one has not been well discussed previously.

Compounds **2a–g** are also fluxional. However, because these compounds undergo ring inversion much more rapidly, only broadening of the peaks in the $^{19}F\{^1H\}$ NMR spectra are observed at low temperatures. No limiting spectra can be obtained even at the lowest accessible temperature -130 °C.

Although these fast exchanging spectra represent merely the average of the interconverting species, detailed spectral analysis provides valuable structural information. For example, the $^{19}F\{^1H\}$ NMR spectrum of **2g** shows two sets of AX spectrum at 133.67, 137.30 and 140.17, 143.37 ppm in spite of being an averaged spectrum of two fast ex-

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[8] Montecalvo, D.; st.-Jacques, M. *J. Am. Chem. Soc.* **1973**, *95*, 2023.
[9] Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.

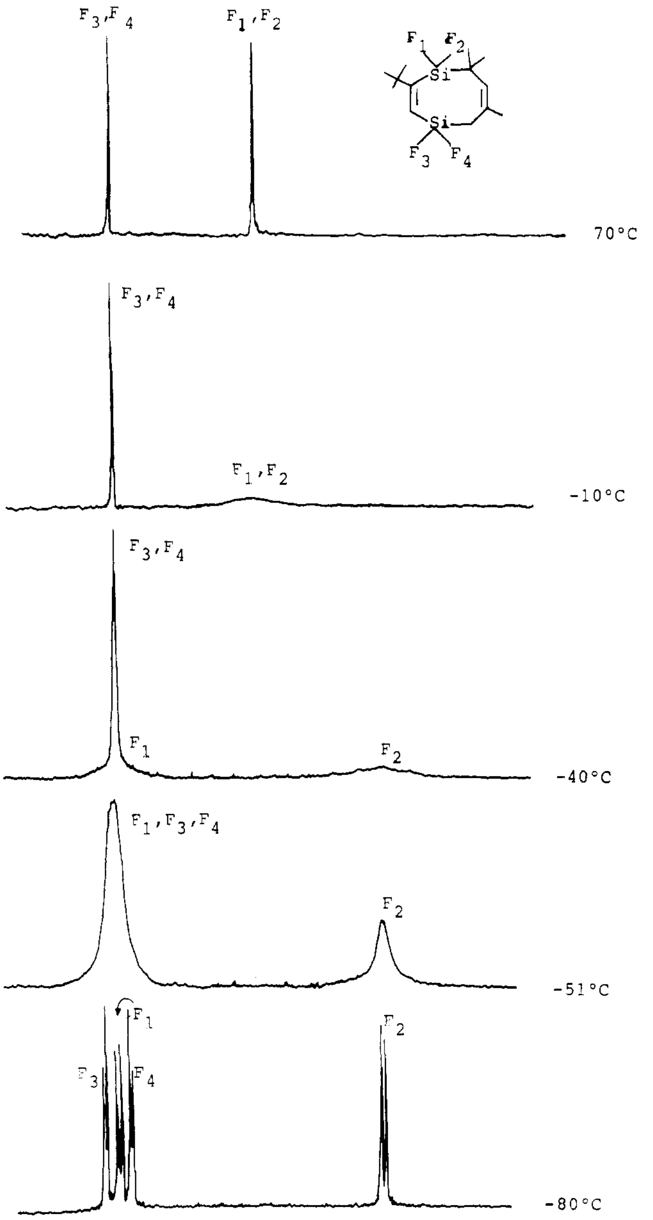
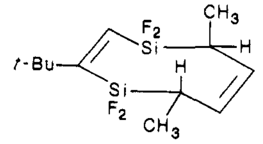


Figure 1. Variable-temperature $^{19}F\{^1H\}_{BB}$ spectra of compound **2i**.

changing conformers. This is because the methyl substitutions on C_5 and C_8 make the fluorines in each of the four SiF_2 groups of the two conformers intrinsically different so that they merge into nonequivalent averaged chemical environments under fast exchange.

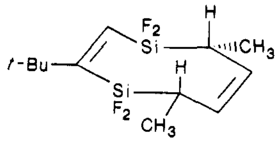
It is interesting to note that a five-bond long-range coupling ($^5J_{F,F}$ = 8 Hz) is indicated by the ^{19}F COSY spectrum. Also, the $^{13}C_{BB}$ spectrum of **2g** shows unusual three-bond coupling ($^3J_{F,C}$ = 4.9 Hz) between F and olefinic carbons C_6 and C_7 (phenomenon also observed in the spectra of **2e**, **2f**, and **2h**). In order to assure that the room-temperature spectra truly represent the time average (but not a mixture) of the two conformers of **2g**, we added a small amount of potassium fluoride in a donor solvent, hexamethylphosphoramide,[10] to the solution of **2g**. The fast exchange of fluorines on the SiF_2 groups "decoupled" the F–C couplings and the previous doublets at δ 130.64 and 129.23 (for C_6 and C_7, respectively) become sharp singlets. These long-range couplings are almost certainly due to the interactions of the corresponding nuclei through close spacial relationship caused by the puckering of the ring.

The relative positions of the two H (hence the two CH_3) on C_5 and C_8 are determined on the basis of following observations: (i) the chemical shifts of the two protons are different (δ 1.80 and 2.10, respectively) and (ii) the selective $^{19}F\{^1H\}$ spectrum shows that the resonances at 133.67 and 143.37 ppm are the ones coupling with the neighboring C*H*, but only the former (133.67 ppm) involves the five-bond F–F coupling. These observations strongly suggest that the two methine hydrogens are cis to each other, one at the equatorial position and the other at the axial position.



2g

For comparison, compound **2h**, the product from the reaction with *trans,trans*-hexa-2,4-diene, shows only one resonance at δ 2.11 for the two methine protons in the ^1H NMR spectrum, and the two methine protons couple with the fluorines at 138.56 and 146.14 ppm, both without a five-bond long-range F–F coupling. So the two methine protons in **2h** are in the "equivalent" positions with respect to the ring skeleton, and they both occupy the axial positions.

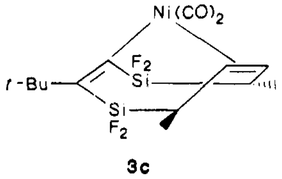


2h

The ^{19}F NMR spectrum of **2h** does not show any change in the range of +100 to −130 °C. It seems likely that the two methyl groups on C_5 and C_8 of **2h** remain at equatorial positions and the preference of diequatorial over diaxial conformation contributes a considerable amount of energy barrier to the process of conformational interconversion.

For the reactions with butadiene derivatives having methyl substitution on C_1 and C_4, intermediates designated as **3** can be observed during the reactions. For example, when the reaction with *trans,trans*-hexadiene was followed by $^{19}F\{^1H\}$ NMR at −60 °C, two sets of AX spectrum at 125.35, 144.16 and 123.02, 143.22 ppm were observed in addition to the spectra of **2h**. These spectra rapidly converted to the spectra of **2h** as the temperature was raised. The conversion was quantitative at 70 °C.

A sample containing mainly the compound responsible for the spectrum mentioned above was sent directly for mass spectrometric analysis, and the mass spectrum showed the parent ion at *m/e* 410 (M^+), which corresponded to the molecular formula $C_{12}H_{20}Si_2F_4Ni(CO)_2$. Since all fluorine chemical shifts are in the region typical for SiF_2 groups attached to organic moieties and no resonance appears in the region typically for SiF_2 groups bonded to metals (80–100 ppm), the $Ni(CO)_2$ group is most likely bound to $C_{12}H_{20}Si_2F_4$ moiety by two metal–olefin bonds. The structure is **3c** as shown.



3c

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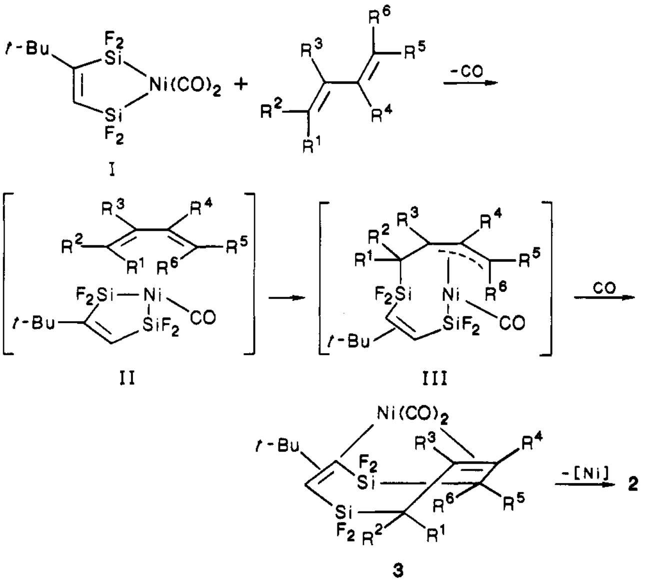
[10] Jzang, T. T. Ph.D. Thesis, National Tsing Hua University, 1987.

Scheme I



Attempts to prepare **3** by reacting the corresponding **2** with $Ni(CO)_4$ photochemically and thermally failed. This may reflect the fact that **2** exists predominately in the chair form in solution.

On the basis of discussion above, a plausible reaction mechanism can be proposed as shown in Scheme I.

All 1,3-butadiene derivatives studied in this work undergo Ni-mediated 1,4-cycloaddition. Intermediates II and III, though not directly observed, are inferred by the existence of **3** as the precursors of **2**. Such intermediates with M = Fe, Cr, Mo, and W were obtained and fully characterized previously.[1-4]

The reactions with *trans*-1,3-pentadiene and *cis*-1,3-pentadiene give **2e** and **2f**, respectively. This observation suggests that the initial attack of SiF_2 is regiospecific. The fact that the reactions with *cis,trans*-hexadiene and *trans,trans*-hexadiene give **2g** and **2h**, respectively, suggests that the second silyl attack is stereospecific. Therefore, the formation of products of stereoselective cycloaddition results from the combination of the regioselectivity of the initial SiF_2 attack in the intermediate II and the complete configuration retention of η^3-allyl moiety in intermediate III.

Experimental Section

Spectra. All mass spectra were recorded on a JEOL JMS-100 mass spectrometer operating at 12 eV. The NMR spectra were obtained from a JEOL JMX-100 spectrometer operating at 99.55, 93.65, and 25.0 MHz for ^1H, ^{19}F and ^{13}C spectra, respectively and a Bruker AM 400 spectrometer operating at 400.0, 376.5, and 100.0 MHz for ^1H, ^{19}F, and ^{13}C spectra, respectively. Chemical shifts of ^1H and ^{13}C were measured in δ values; ^{19}F chemical shifts were measured in parts per million upfield from internal standard CCl_3F. For the ^{13}C data listed below, the spectral multiplicity following each chemical shift is due to the coupling with heteronuclei, whereas the coupling patterns in $^{13}C\{^1H\}_{CW}$ are included in the parentheses.

Preparation of 3-*tert*-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) and $F_2\overline{Si(t\text{-}Bu)C{=}CHSiF_2Ni}(CO)_2$ (I). Compound **1** was prepared by the cocondensation reaction between *tert*-butylacetylene and difluorosilylene.[11] Compound I was prepared by the reaction between **1** and $Ni(CO)_4$. A typical run is described as follows: 0.43 g (2.0 mmol) of **1** in a 10-mL *n*-pentane solution was transferred to a quartz tube under vacuum before 0.6 g (3.5 mmol) of $Ni(CO)_4$ was added. The sealed reaction tube was irradiated (medium-pressure Hg lamp) at −30 °C and subjected to degassing every 30 min. Compound **1** was consumed in about 6 h. After the solvent and excess $Ni(CO)_4$ were pumped 5 mL of dried chloroform was added. The solution was kept at −30 °C for 12 h to complete the precipitation of a black solid. After filtration and concentration under vacuum, 0.6 g (1.8 mmol) of compound I was obtained with a 90% yield. The characterization of I was reported previously.[12]

Preparation of 1,1,4,4-Tetrafluoro-1,4-disilacycloocta-2,6-diene Derivatives (2 Family). Compounds designated by **2** were prepared by reacting I and the corresponding diene $R^1R^2C{=}CR^3CR^4{=}CR^5R^6$ (R = H or CH_3). A typical run is described as follows: 0.6 g (1.8 mmol) of I and 3.0 mmol of a diene in a 10-mL *n*-pentane solution was degassed and sealed in a reaction tube. The solution was kept at −30 °C for 6 h. After removal of solvent and excess diene, 2 mL of dried isooctane was added. The solution was heated to 120 °C for 30 min and then subjected to concentration and distillation under vacuum: about 1.2 mmol of the corresponding **2** was obtained with a yield of 50–80%.

(i) **2a** from the reaction with 1,3-butadiene: yield 80%. Anal. Calcd for **2a**: C, 44.77; H, 5.97; F, 28.36. Found: C, 44.30; H, 6.15; F, 28.51. Mass spectrum of **2a**: *m/e* 268 (M^+, $C_{10}H_{16}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$), 54 ($C_4H_6^+$). ^1H NMR of **2a**: δ 1.16 (s, 9 H, *t*-Bu), 1.92 (c, 4 H, two $-CH_2-$), 5.52 (c, 2 H, $-\mathit{H}C{=}C\mathit{H}-$), 6.36 (t, 1 H, $=C\mathit{H}SiF_2-$). $^{19}F\{^1H\}$ NMR of **2a**: 127.26 (c) and 134.63 (c) ($=CHSi\mathit{F}_2-$ and $=C(t\text{-}Bu)Si\mathit{F}_2$, respectively). Assignment of the two SiF_2 groups are determined by selective proton-decoupled ^{19}F spectrum irradiating at $=C\mathit{H}SiF_2-$. ^{13}C NMR of **2a**: δ 167.34 (m, (m), $=\mathit{C}(t\text{-}Bu)SiF_2-$), 130.37 (m (d, m), $=\mathit{C}HSiF_2-$), 122.70 (s (d)) and 122.20 (s (d)) ($-H\mathit{C}{=}\mathit{C}H-$), 39.49 (s (s), $-\mathit{C}(CH_3)_3$), 28.89 (s (q), $-C(\mathit{CH}_3)_3$), 15.06 (t (c)) and 14.47 (t (c)) (two $-\mathit{C}H_2-$).

(ii) **2b** from the reaction with 2,3-dimethylbuta-1,3-diene; yield 80%. Anal. Calcd for **2b**: C, 48.64; H, 6.76; F, 25.67. Found: C, 48.50; H, 6.31; F, 25.58. Mass spectrum of **2b**: *m/e* 296 (M^+, $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 252 ($C_9H_{12}Si_2F_4^+$), 240 ($C_8H_{12}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 82 ($C_6H_{10}^+$), 57 ($C_4H_9^+$). ^1H NMR of **2b**: δ 1.12 (s, 9 H, *t*-Bu), 1.68 (s, 6 H, $-C(C\mathit{H}_3){=}C(C\mathit{H}_3)-$), 1.86 (c, 4 H, two $-CH_2-$), 6.32 (t, 1 H, $=C\mathit{H}SiF_2-$). $^{19}F\{^1H\}$ NMR of **2b**: δ 125.13 (c) and 132.24 (c) ($=CHSiF_2-$ and $=C(t\text{-}Bu)SiF_2-$, respectively). Assignment determined by selective proton-decoupled ^{19}F spectrum irradiating at $=C\mathit{H}SiF_2-$. ^{13}C NMR of **2b**: δ 167.98 (t, t (t, t), $=\mathit{C}(t\text{-}Bu)$), 130.72 (m (d, m), $=\mathit{C}HSiF_2-$), 121.87 (s (s)) and 121.64 (s (s)) ($-\mathit{C}(CH_3){=}\mathit{C}(CH_3)-$), 39.32 (s (s), $-\mathit{C}(CH_3)_3$), 29.00 (s (q), $-C(\mathit{C}H_3)_3$), 23.14 (t (t, t), two $-\mathit{C}H_2-$), 21.50 (s (q)) and 20.86 (s (q)) ($-C(\mathit{C}H_3){=}C(\mathit{C}H_3)-$).

(iii) **2c** and **2d** (1:1 ratio) from the reaction with isoprene; yield 80%. Anal. Calcd for **2c/2d**: C, 46.81; H, 6.38; F, 26.95. Found: C, 46.50; H, 6.52; F, 26.82. Mass spectrum of **2c/2d**: *m/e* 282 (M^+, $C_{11}H_{18}Si_2F_4^+$), 267 ($C_{10}H_{16}Si_2F_4^+$), 225 ($C_7H_9Si_2F_4^+$), 212 ($C_6H_8Si_2F_4^+$), 57 ($C_4H_9^+$). ^1H NMR of **2c/2d**: δ 1.13 (s, 18 H, two *t*-Bu), 1.72 (s, 6 H, $=C(CH_3)-$ of **2c** and **2d**), 1.86 (c, 8 H, four $-CH_2-$ of **2c** and **2d**), 5.21 (t, 2 H, $=C\mathit{H}CH_2-$ of **2c** and **2d**), 6.30 (t) and 6.34 (t) (2 H, $=C\mathit{H}SiF_2-$ of **2c** and **2d**). $^{19}F\{^1H\}$ NMR of **2c/2d**: δ 125.77 (c) and 133.52 (c), 126.86 (c) and 134.20 (c) ($=CHSiF_2-$ and $=C(t\text{-}Bu)SiF_2-$ of **2c** and /or **2d**). ^{13}C NMR of **2c/2d**: δ 168.39 (m (m), $=\mathit{C}(t\text{-}Bu)$), 131.13 (m (d, m), $=\mathit{C}HSiF_2-$ of **2c** or **2d**), 131.10 (s (s), $=\mathit{C}(CH_3)-$), 129.90 (m (d, m), $=\mathit{C}HSiF_2-$ of **2d** or **2c**), 115.54 (s (d), $=\mathit{C}HCH_2-$), 39.55 (s (s)) and 39.26 (s (s)) ($-\mathit{C}(CH_3)_3$ of **2c** and **2d**), 28.95 (s (q), $-C(\mathit{C}H_3)_3$), 26.25 (s (q)) and 25.61 (s (q)) ($=C(\mathit{C}H_3)-$ of **2c** and **2d**); 20.51 (t (m)) 19.63 (t (m)), and 15.35 (t (m)) (all $-\mathit{C}H_2-$ in **2c** and **2d**).

(iv) **2e** from the reaction with *trans*-pentadiene; yield 65%. Anal. Calcd for **2e**: C, 46.8; H, 6.38; F, 26.95. Found: C, 46.44; H, 6.01; F, 26.91. Mass spectrum of **2e**: 282 (M^+, $C_{11}H_{18}Si_2F_4^+$), 267 ($C_{10}H_{16}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 129 ($C_6H_{10}SiF^+$), 57 ($C_4H_9^+$). ^1H NMR of **2e**: δ 1.12 (s, 9 H, *t*-Bu), 1.28 (d, 3 H, $-CH(C\mathit{H}_3)-$), 1.84 (m, 2 H, CH_2), 2.10 (m, 1 H, $-C\mathit{H}(CH_3)-$), 5.32 (t, 1 H, $=C\mathit{H}CH(CH_3)-$), 5.38 (q, 1 H, $=C\mathit{H}CH_2-$), 6.36 (m, 1 H, $=C\mathit{H}SiF_2-$). $^{19}F\{^1H\}$ NMR of **2e**: δ 136.48 (d) and 128.16 (d, d) ($=CHSiF_2CH(CH_3)-$), 136.65 and 132.66 ($=C(t\text{-}Bu)Si\mathit{F}_2CH_2-$).

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(11) Liu, C. S.; Margrave, J. L.; Thompson, J. C. *Can. J. Chem.* **1972**, *50*, 465.

(12) Cheng, C. W.; Liu, C. S. *J. Am. Chem. Soc.* **1975**, *97*, 6746.

Assignments of the two SiF$_2$ groups and their relative positions in the ring are determined by selective proton-decoupled ^{19}F spectra irradiating at =C*H*SiF$_2$, –C*H*(CH$_3$)–, and –C*H*$_2$–. ^{13}C NMR of **2e**: δ 167.58 (t (t), =*C*(*t*-Bu)), 131.36 (d (d, d)) and 121.35 (d (d, d)) (–H*C*=*C*H–), 130.01 (t (d, t), =*C*HSiF$_2$), 39.37 (s (s), *C*(CH$_3$)$_3$), 29.12 (s (q), C(*C*H$_3$)$_3$), 20.86 (m (d, m), –*C*H(CH$_3$)–), 14.92 (t (t, t), –*C*H$_2$–), 13.30 (s (q), –CH(*C*H$_3$)–).

(v) **2f** from the reaction with *cis*-pentadiene; yield 70%. Anal. Calcd for **2f**: C, 46.8; H, 6.38; F, 26.95. Found: C, 46.27; H, 6.15; F, 26.80. Mass spectrum of **2f**: similar to that of **2e**. ^{1}H NMR of **2f**: δ 1.12 (s, 9 H, *t*-Bu), 1.27 (d), 3 H, –CH(C*H*$_3$)–), 1.62 (m, 2 H, –CH$_2$–), 1.90 (m, 1 H, –C*H*(CH$_3$)–), 5.34 (t, 1 H, =C*H*CH(CH$_3$)–), 5.42 (c, 1 H, =C*H*CH$_2$–), 6.37 (m, 1 H, =C*H*SiF$_2$–). ^{19}F{^{1}H} NMR of **2f**: 132.88 (d) and 123.00 (d, d, =CHSiF$_2$CH$_2$–), 145.51 (d) and 137.80 (d, d) (=C(*t*-Bu)SiF$_2$CH(CH$_3$)–). Assignments of the two SiF$_2$ and their relative position in the ring are determined by selective proton-decoupled ^{19}F spectra irradiating at =C*H*SiF$_2$, –C*H*(CH$_3$)–, and –CH$_2$–. ^{13}C NMR of **2f**: δ 166.75 (t (t), =*C*(*t*-Bu)), 131.43 (d (d, d)) and 120.85 (d (d, d)) (–H*C*=*C*H–), 130.63 (t (d, t), =*C*HSiF$_2$–), 39.55 (s (s), *C*(CH$_3$)$_3$), 29.00 (s (q), C(*C*H$_3$)), 20.45 (m (d, m), –*C*H(CH$_3$)–), 15.46 (t (t, t), –*C*H$_2$–), 12.89 (s (q), –CH(*C*H$_3$)–).

(vi) **2g** from the reaction with *cis*-2,*trans*-4-hexadiene; yield 65%. Anal. Calcd for **2g**: C, 48.65; H, 6.76; F, 25.67. Found: C, 48.22; H, 6.49; F, 25.58. Mass spectrum of **2g**: *m*/*e* 296 (M$^+$, $\mathrm{C_{12}H_{20}Si_2F_4^+}$), 281 ($\mathrm{C_{11}H_{17}Si_2F_4^+}$), 254 ($\mathrm{C_9H_{14}Si_2F_4^+}$), 215 ($\mathrm{C_6H_{11}Si_2F_4^+}$), 129 ($\mathrm{C_6H_{10}SiF^+}$), 57 ($\mathrm{C_4H_9^+}$). ^{1}H NMR of **2g**: δ 1.10 (s, 9 H, *t*-Bu), 1.18 (d) and 1.19 (d) (6 H, two –CH(C*H*$_3$)–), 1.80 (m) and 2.10 (m) (2 H, two –C*H*(CH$_3$)–), 5.24 (m) (2 H, –*H*C=C*H*–), 6.38 (m, 1 H, =C*H*SiF$_2$–). ^{19}F{^{1}H} NMR of **2g**: δ 137.30 (d) and 133.67 (d, d) (=CHSi*F*$_2$–), 143.37 (d) and 140.17 (d, d) (=C(*t*-Bu)SiF$_2$–). Assignments of the two SiF$_2$ groups, their relative positions in the ring, and the relative spacial orientations of the two methyl groups are determined by selective proton-decoupled ^{19}F spectra irradiating at =C*H*SiF$_2$– and two –C*H*(CH$_3$)– (at δ 1.80 and 2.10, respectively). ^{13}C NMR of **2g**: δ 167.92 (t (t), =*C*(*t*-Bu)), 130.64 (d (d, d)) and 129.23 (d (d, d)) (–H*C*=*C*H–), 130.22 (t (d, t), =*C*HSiF$_2$), 39.49 (s (s), –*C*(CH$_3$)$_3$), 29.00 (s (q), –C(*C*H$_3$)$_3$), 20.56 (m (d, m) and 19.98 (m (d, m) (two –*C*H(CH$_3$)–), 12.89 (s (q)) and 12.48 (s (q)) (two –CH(*C*H$_3$)–).

(vii) **2h** from the reaction with *trans*-2,*trans*-4-hexadiene; yield 65%. Anal. Calcd for **2h**: C, 48.65; H, 6.76; F, 25.67. Found: C, 48.80; H, 6.48; F, 25.50. Mass spectrum of **2h**: similar to that of **2g**. ^{1}H NMR of **2h**: δ 1.10 (s, 9 H, *t*-Bu), 1.19 (d) and 1.27 (d) (6 H, two –CH(C*H*$_3$)–), 2.11 (m, 2 H, two –C*H*(CH$_3$)–), 5.12 (t, 2 H, –*H*C=C*H*–), 6.28 (m, 1 H, =C*H*SiF$_2$–). ^{19}F{^{1}H} NMR of **2h**: δ 138.52 (d) and 122.97 (d, d) (=CHSi*F*$_2$), 146.14 (d) and 136.57 (d, d) (=(*t*-Bu)Si*F*$_2$–). Assignments of the two SiF$_2$ groups, their relative positions in the ring, and the relative spacial arrangement of the two methyl groups are determined by selective proton-decoupled ^{19}F NMR irradiating at =C*H*SiF$_2$– and two –C*H*(CH$_3$)– (both at δ 2.11). ^{13}C NMR of **2h**: δ 166.46 (t (t), =*C*(*t*-Bu)SiF$_2$), 130.26 (d (d, d)) and 129.37 (d (d, d)) (–H*C*=*C*H–), 134.88 (t (d, t), =*C*HSiF$_2$–), 38.96 (s (s),–*C*(CH$_3$)$_3$), 28.88 (s (q), –C(*C*H$_3$)$_3$), 21.44 (m (d, m), two –*C*H(CH$_3$)–), 13.94 (s (q)) and 12.83 (s (q)) (two –CH(*C*H$_3$)–).

(viii) **2i** from the reaction with 2,4-dimethylpenta-1,3-diene, yield 50%. Anal. Calcd for **2i**: C, 50.32; H, 7.09; F, 24.52. Found: C, 49.98; H, 6.84; F, 24.15. Mass spectrum of **2i**: *m*/*e* 310 (M$^+$, $\mathrm{C_{13}H_{22}Si_2F_4^+}$), 295 ($\mathrm{C_{12}H_{19}Si_2F_4^+}$), 253 ($\mathrm{C_9H_{13}Si_2F_4^+}$), 215 ($\mathrm{C_6H_{11}Si_2F_4^+}$), 149 ($\mathrm{C_6H_{11}SiF_2^+}$), 57 ($\mathrm{C_4H_9^+}$). ^{1}H NMR of **2i**: δ 1.12 (s, 9 H, *t*-Bu), 1.19 (s, 6 H, –C(CH$_3$)$_2$–), 1.71 (s, 3 H, =C(C*H*$_3$)–), 2.15 (m, –CH$_2$–), 4.93 (br s, 1 H, =C*H*C(CH$_3$)$_2$–), 6.45 (m, 1 H, =C*H*SiF$_2$–). ^{19}F{^{1}H} NMR of **2i**: δ 127.43 (s) and 138.12 (br), time-averaged spectrum of the two SiF$_2$ groups. ^{19}F{^{1}H} slow-exchange-limiting spectra of **2i** at −80 °C: δ 128.20 (d) and 126.11 (d) (=C(*t*-Bu)Si*F*$_2$–), 127.26 (d) and 144.93 (d) (=CHSi*F*$_2$–). Assignments of the two SiF$_2$ groups and their relative positions in the ring are determined by selective proton-decoupled ^{19}F spectra irradiating at =C*H*SiF$_2$– and –C*H*$_2$–. ^{13}C NMR of **2i**: δ 168.98 (m (m), =*C*(*t*–Bu)), 133.30 (s (d), =*C*HC(CH$_3$)$_2$–) 131.36 (t (d, t), =*C*HSiF$_2$–), 127.73 (s (s), =*C*(CH$_3$)–), 39.66 (s (s), –*C*(CH$_3$)$_3$), 29.35 (s (q), –C(*C*H$_3$)$_3$), 26.37 (s (q), =C(*C*H$_3$)–), 24.61 (s (q), –C(*C*H$_3$)$_2$–), 23.91 (t (t,t), –*C*H$_2$–), 18.80 (t (t), –*C*(CH$_3$)$_2$–).

Preparation of (η^4-1,4-Disilacycloocta-2,6-diene)Ni(CO)$_2$ (3 Family). Intermediate compounds **3** were observed at low temperature in the early stage of the reactions which led to the formation of the final products **2**. None of these compounds were stable enough for isolation and full characterization. However, some gave satisfactary mass spectra and ^{19}F NMR spectra. One characteristic of the metal-fixed boat conformation of these compounds is the large geminal F–F coupling, being in the range of 32–35 Hz. The ^{19}F NMR spectra of **3** were obtained by subtracting the spectra of the corresponding **2** from the mixture. Subtracted ^{1}H spectra were much less meaningful because of heavy spectral overlapping. ^{13}C NMR spectra were not obtained due to the instability of **3**.

(i) Mass spectrum of **3a** (from the reaction with *trans*-1,3-pentadiene): *m*/*e* 396 (M$^+$, $\mathrm{C_{11}H_{18}Si_2F_4Ni(CO)_2^+}$), 368 ($\mathrm{C_{11}H_{18}Si_2F_4Ni(CO)^+}$), 340 ($\mathrm{C_{11}H_{18}Si_2F_4Ni^+}$), 282 ($\mathrm{C_{11}H_{18}Si_2F_4^+}$), 267 ($\mathrm{C_{11}H_{15}Si_2F_4^+}$), 215 ($\mathrm{C_6H_{11}Si_2F_4^+}$), 57 ($\mathrm{C_4H_9^+}$). ^{19}F{^{1}H} NMR of **3a**: δ 123.17 and 142.66 (AX) (=C(*t*-Bu)SiF$_2$–), 122.21 and 136.48 (AX) (=CHSiF$_2$–).

(ii) Mass spectrum of **3b** (from the reaction with *cis*-1,3-pentadiene): similar to that of **3a**. ^{19}F{^{1}H} NMR of **3b**: δ 133.12 and 145.23 (AX) (=C(*t*-Bu)SiF$_2$–), 127.18 and 143.79 (AX) (=CHSiF$_2$–).

(iii) Mass spectrum of **3c** (from the reaction with *trans*,*trans*-hexadiene): *m*/*e* 410 (M$^+$, $\mathrm{C_{12}H_{20}Si_2F_4Ni(CO)_2^+}$), 382 ($\mathrm{C_{12}H_{20}Si_2F_4Ni(CO)^+}$), 354 ($\mathrm{C_{12}H_{20}Si_2F_4Ni^+}$), 296 ($\mathrm{C_{12}H_{20}Si_2F_4^+}$), 281 ($\mathrm{C_{11}H_{17}Si_2F_4^+}$), 254 ($\mathrm{C_9H_{14}Si_2F_4^+}$), 215 ($\mathrm{C_6H_{11}Si_2F_4^+}$), 129 ($\mathrm{C_6H_{10}SiF^+}$), 57 ($\mathrm{C_4H_9^+}$). ^{19}F{^{1}H} NMR of **3c**: δ 125.35 and 144.16 (AX) (=C(*t*-Bu)SiF$_2$–), 123.02 and 143.22 (AX) (=CHSiF$_2$–).

(iv) Mass spectrum of **3d** (from the reaction with *cis*,*trans*-hexadiene: similar to that of **3c**. ^{19}F{^{1}H} NMR of **3d**: δ 132.23 and 145.23 (AX) (=C(*t*-Bu)SiF$_2$–), 123.92 and 137.77 (AX) (=CHSiF$_2$–).

(v) Mass spectrum of **3e** (form the reaction with 2,4-dimethylpenta-1,3-diene): *m*/*e* 424 (M$^+$, $\mathrm{C_{13}H_{22}Si_2F_4Ni(CO)_2^+}$), 396 ($\mathrm{C_{13}H_{22}Si_2F_4Ni(CO)^+}$), 368 ($\mathrm{C_{13}H_{22}Si_2F_4Ni^+}$), 310 ($\mathrm{C_{13}H_{22}Si_2F_4^+}$), 295 ($\mathrm{C_{12}H_{19}Si_2F_4^+}$), 254 ($\mathrm{C_9H_{14}Si_2F_4^+}$), 149 ($\mathrm{C_6H_{11}SiF_2^+}$), 57 ($\mathrm{C_4H_9^+}$). ^{19}F{^{1}H} NMR of **3e**: δ 128.11 and 142.28 (AX) (=C(*t*-Bu)SiF$_2$–), 119.20 and 142.28 (AX) (=CHSiF$_2$–).

Acknowledgment. The financial support to this work by the National Science Council of the Republic of China is acknowledged with gratitude. T.T.J. thanks the Ministry of Education for a postgraduate fellowship. C.Y.L. thanks the NSC for a postdoctoral fellowship.

Registry No. 1, 36091-97-1; **2a**, 109034-51-7; **2b**, 109034-52-8; **2c**, 113794-95-9; **2d**, 113794-96-0; **2e**, 113794-97-1; **2f**, 113810-76-7; **2g**, 113794-99-3; **2h**, 113794-98-2; **2i**, 113857-73-1; **3a**, 113857-74-2; **3b**, 113892-35-6; **3c**, 113857-75-3; **3d**, 113972-60-4; **3e**, 113857-76-4; I, 55500-76-0; Ni(CO)$_4$, 13463-39-3; 1,3-butadiene, 106-99-0; 2,3-dimethyl-1,3-butadiene, 513-81-5; isoprene, 78-79-5; *trans*-1,3-pentadiene, 2004-70-8; *cis*-1,3-pentadiene, 1574-41-0; *trans*,*trans*-hexadiene, 5194-51-4; *cis*,*trans*-hexadiene, 5194-50-3; 2,4-dimethylpenta-1,3-diene, 1000-86-8.